

TITLE

TWO-COMPONENT COATING COMPOSITIONS

PRIORITY

5 This application claims priority from Provisional U.S. Patent Application
Serial No. 60/451,446, filed March 3, 2003, incorporated herein by reference.

Background of the Invention

Field of the Invention

10 The invention relates to solvent-based two-component coating compositions comprising hydroxy-functional lactone-modified (meth)acrylic copolymers and polyisocyanate hardeners that are useful for automotive and industrial coatings.

15	<u>Description of Related Art</u>
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In automotive coatings in particular, there is a need for two-component coating compositions which produce scratch resistant and chemical resistant coatings. It is already known from the prior art that scratch resistant coatings can be obtained in general by using hydroxy-functional (meth)acrylic copolymers whose hydroxyl groups are modified with lactones. But in addition to good scratch resistance, these coating compositions require the development on curing of good hardness and are required to have balanced physical drying properties.

For example, coating compositions for automotive coatings that are based on lactone-modified (meth)acrylic copolymers and polyisocyanate cross-linking agents are described in EP-A-1 227 113. The (meth)acrylic copolymers are prepared from pre-adducts of lactones and hydroxyalkyl(meth)acrylates and additional unsaturated monomers. The scratch resistance of the coatings achieved with these compositions still requires improvement.

US Patent 3,892,714 describes hydroxyfunctional (meth)acrylic copolymers with main and side chains whereby the main chains comprise a

copolymer of ethylenically unsaturated monomers, at least one of which contains hydroxyl groups, and the side chains comprise lactone chains attached to said hydroxyl groups. The copolymers may be prepared and subsequently modified with the lactone or the side chain may be attached to an ethylenically unsaturated hydroxy monomer and the copolymer is then prepared by polymerization with other unsaturated monomers. The amount of lactone added is from 10-60 weight %, related to the weight of the unmodified copolymer. Besides hydroxy functional unsaturated monomers styrene, vinyl toluene, methyl methacrylate, vinyl acetate and butyl methacrylate are preferably used as other monomers. Disadvantages of these coating compositions are poor hardness development, poor physical drying performance and the compositions still have insufficient scratch resistance.

WO-A-00/37524 is directed to coating compositions based on acrylic polyols that are the polymerization products of 20-70 weight % of hydroxy functional (meth)acrylate monomers and 30-80 weight % of (meth)acrylate monomers without hydroxyl groups, wherein hydroxy functional (meth)acrylate monomers comprising 0.5-15 weight % of a (meth)acrylate in which the esterifying group is the residue of a glycidyl group and includes a branched alkyl group, preferably reaction products of (meth)acrylic acid with glycidyl esters of saturated alpha, alpha'-dialkylalkane monocarboxylic acids having 7 to 13 carbon atoms in the molecule, 5-40 weight % of a (meth)acrylate in which the esterifying group is a hydroxy ester having one or more ester groups, preferably adducts of hydroxy alkyl (meth)acrylates and lactones and 0-40 weight % of other hydroxy functional monomers. These coating compositions develop insufficient hardness but have insufficient scratch resistance.

EP-A-1 201 690 relates to hydroxyfunctional methacrylic copolymers containing epoxyfunctional unsaturated monomers, compounds with carboxyl and hydroxyl groups being reacted with the epoxy functional groups of the unsaturated monomers, and additional unsaturated monomers. Optionally, the polymer can be reacted with a lactone. Disadvantages of coating

compositions based on these copolymers and polyisocyanate hardeners are poor drying performance and insufficient hardness.

Accordingly, there is a need for automotive clear coat compositions which not only have very good scratch resistance but also meet requirements for excellent physical drying properties and hardness development, especially after drying at relatively low temperatures (e.g. below 80°C).

Summary of the Invention

The invention is directed to two-component coating compositions comprising

A) at least one hydroxy-functional (meth)acrylic copolymer having an OH value from 160 to 200 mg KOH/g and a weight average molecular weight Mw from 2,500 to 30,000 and

B) at least one polyisocyanate cross-linking agent;

wherein the hydroxy-functional (meth)acrylic copolymer A) is obtained by A1) free-radically copolymerizing a monomer mixture comprising

a) at least one hydroxy functional free-radically copolymerizable olefinically unsaturated monomer,

b) at least one cycloaliphatic ester of a free-radically copolymerizable olefinically unsaturated carboxylic acid and

c) at least one additional free-radically copolymerizable olefinically unsaturated monomer which is different from component a) and b) and

All) reacting at least part of the hydroxyl groups of the hydroxy-functional (meth)acrylic copolymer obtained in step A1) with

d) at least one lactone compound;

wherein the hydroxy-functional (meth)acrylic copolymer obtained in step A1) has a glass transition temperature Tg of at least 50°C and wherein said copolymer is free of epoxy-functional free-radically copolymerizable olefinically unsaturated monomers.

Detailed Description of the Embodiments

The term (meth)acrylic as used here and hereinafter should be taken to mean methacrylic and/or acrylic. Wt-% should be taken to mean weight percent.

5 Surprisingly, it was found that hydroxy-functional (meth)acrylic copolymers prepared in this way, when used in coating compositions with isocyanate-crosslinker, form coatings having in particular a balanced ratio among excellent scratch resistance, good hardness development and physical drying performance.

10 Preferred hydroxy-functional (meth)acrylic copolymers A) have an OH value from 170 to 190 mg KOH/g and a weight average molecular weight Mw from 2,500 to 20,000.

Preferred hydroxy-functional (meth)acrylic copolymers obtained in step A1) have an OH value from 170 to 280 mg KOH/g, a weight average molecular weight Mw from 2,000 to 20,000 and an acid value of 0 to 40 mg KOH/g. The
15 glass transition temperature Tg of said copolymer is preferably from 60°C to 100°C. The glass transition temperature of the copolymer has been calculated from the glass transition temperature of the homopolymers of the monomers according to the Flory-Fox equation. Glass transition
20 temperatures of the homopolymers have been determined by differential scanning calorimetry (DSC).

In the following, the invention will be described in more detail. The hydroxy-functional (meth)acrylic copolymers A) comprise preferably 30-60 wt-% of component a), 15-40 wt-% of component b), 10-40 wt-% of component c)
25 and 18-40 wt-%, most preferably 20-30 wt-% of component d), wherein the proportions by weight of components a) to d) totaling 100 wt-%.

Examples of suitable hydroxy-functional olefinically unsaturated monomers (component a) are hydroxyalkyl esters of alpha, beta-olefinically unsaturated monocarboxylic acids having primary or secondary hydroxyl
30 groups. Examples include the hydroxyalkyl esters of acrylic acid, methacrylic acid, crotonic acid and/or isocrotonic acid. The hydroxyalkyl esters of (meth)acrylic acid are preferred. The hydroxyalkyl radicals may contain, for

example, 1 to 10 carbon atoms, preferably 2 to 6 carbon atoms. Examples of suitable hydroxyalkyl esters of alpha, beta-olefinically unsaturated monocarboxylic acids having primary hydroxyl groups are hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, hydroxyamyl (meth)acrylate, and hydroxyhexyl (meth) acrylate. Examples of suitable hydroxyalkyl esters having secondary hydroxyl groups are 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, and 3-hydroxybutyl (meth) acrylate.

Further hydroxy-functional unsaturated monomers which may be used are reaction products of alpha, beta-unsaturated monocarboxylic acids with glycidyl esters of saturated monocarboxylic acids branched in the alpha position, e.g., with glycidyl esters of saturated alpha-alkylalkane monocarboxylic acids or alpha,alpha'-dialkylalkane monocarboxylic acids. These are preferably the reaction products of (meth)acrylic acid with glycidyl esters of saturated alpha,alpha'-dialkylalkane monocarboxylic acids having 7 to 13 carbon atoms in the molecule, particularly preferably having 9 to 11 carbon atoms in the molecule. Other hydroxy-functional unsaturated monomers are polyethylene oxide and/or polypropylene oxide modified (meth)acrylates.

Examples of suitable cycloaliphatic esters of olefinically unsaturated carboxylic acids (component b) are cycloaliphatic esters of olefinically unsaturated carboxylic acids with cycloaliphatic alcohols. Examples of suitable olefinically unsaturated carboxylic acids include acrylic acid, methacrylic acid, crotonic acid and isocrotonic acid. The alcohols are, in particular, cycloaliphatic monohydric branched or unbranched alcohols having 1-20 carbon atoms in the molecule. Component c) concerns preferably cycloaliphatic esters of (meth)acrylic acid. The cycloaliphatic (meth)acrylates may also be substituted. The substituents are, for example, one or more, e.g., up to three alkyl groups, particularly those having 1-4 carbon atoms. Preferred examples for cycloaliphatic esters of (meth)acrylic acid are cyclohexyl acrylate, trimethylcyclohexyl acrylate, 4-tert. butylcyclohexyl acrylate, isobornyl acrylate and the corresponding methacrylates.

The additional olefinically unsaturated monomers capable of radical polymerization of component c) are any olefinically unsaturated monomers capable of free-radical polymerization, which are different from a) and b) with exception of epoxy-functional free-radically copolymerizable olefinically unsaturated monomers. Examples of additional suitable unsaturated monomers may contain apart from an olefinic double bond further functional groups or may contain apart from an olefinic double bond no further functional groups. Component c) preferably comprises: olefinically unsaturated carboxylic acids capable of free-radical polymerization, aliphatic esters of olefinically unsaturated carboxylic acids capable of free-radical polymerization, vinyl ester and /or vinylaromatic hydrocarbons.

Examples of suitable olefinically unsaturated carboxylic acids include acrylic acid, methacrylic acid, crotonic acid and isocrotonic acid. Acrylic and methacrylic acid are preferred. Examples of suitable aliphatic esters of olefinically unsaturated carboxylic acids capable of free-radical polymerization include, in particular, esters of alpha,beta-olefinically unsaturated monocarboxylic acids with aliphatic alcohols. Examples of suitable olefinically unsaturated carboxylic acids are the above mentioned acids. The alcohols are, in particular, aliphatic monohydric branched or unbranched alcohols having 1-20 carbon atoms in the molecule. Examples of (meth)acrylates with aliphatic alcohols are methyl acrylate, ethyl acrylate, isopropyl acrylate, tert.-butyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate, stearyl acrylate and the corresponding methacrylates.

Examples of suitable vinyl esters are vinyl acetate, vinyl propionate and vinyl esters of saturated monocarboxylic acids branched in the alpha position, e.g., vinyl esters of saturated alpha,alpha'-dialkylalkane monocarboxylic acids and vinyl esters of saturated alpha-alkylalkane monocarboxylic acids having in each case 5-13 carbon atoms, preferably 9-11 carbon atoms in the molecule.

Examples of vinylaromatic hydrocarbons preferably are those having 8-12 carbon atoms in the molecule. Examples of such monomers are styrene, alpha-methylstyrene, chlorostyrenes, vinyltoluenes, 2,5-dimethylstyrene, p-

methoxystyrene and tertiary-butylstyrene. Most preferred styrene is used as component c).

Examples of other additional suitable unsaturated monomers, which contain apart from an olefinic double bond further functional groups are urea, amine, amide, acetoacetate, sulfonic acid, silane and imidazole functional
5 unsaturated monomers as ethyleneurea ethyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, acetoacetoxyethyl (meth)acrylate, (meth)acrylamide, alkoxy methyl (meth)acrylamides, vinyl silane, methacryloxyethyl trialkoxysilanes, acrylamido 2 – methyl propane, sulfonic
10 acid, vinyl imidazole.

Examples of suitable lactones (component d) are those containing 3 to 15 carbon atoms in the ring and where the rings may also have various substituents. Preferred lactones are gamma butyrolactone, delta valerolactone, epsilon caprolactone, beta-hydroxy-beta-methyl-delta
15 valerolactone, lambda laurilactone or mixtures thereof. Epsilon caprolactone is particularly preferred.

The hydroxy-functional (meth)acrylic copolymers A) do not contain epoxy-functional olefinically unsaturated monomers capable of free-radical polymerization.

20 According to the invention, it is essential that the hydroxy-functional (meth)acrylic copolymers A) are obtained by copolymerizing monomers a) to c) (step AI) and reacting at least a part of the hydroxyl groups of the resultant copolymer obtained in step AI) with component d) (step AII).

The preparation of the hydroxy-functional (meth)acrylic copolymer in
25 step AI) takes place by radical copolymerization. This may be carried out in a manner known to the skilled person by conventional processes, particularly by radical solution polymerization using radical initiators. Examples of suitable radical initiators are dialkyl peroxides, diacyl peroxides, hydroperoxides such as cumene hydroperoxide, peresters, peroxydicarbonates, perketals, ketone
30 peroxides, azo compounds, such as, 2,2'-azo-bis-(2,4-dimethylvaleronitrile), azo-bis-isobutyronitrile, C-C-cleaving initiators, such as, e.g., benzpinacol

derivatives. The initiators may be used in amounts from 0.1 to 4.0 wt-%, for example, based on the initial monomer weight.

The solution polymerization process is generally carried out in such a way that the solvent is charged to the reaction vessel, heated to the boiling
5 point and the monomer/initiator mixture is metered in continuously over a particular period. Polymerization is carried out preferably at temperatures between 60°C and 200°C and more preferably at 130°C to 180°C.

Examples of suitable organic solvents which may be used advantageously in solution polymerization and also later in the coating
10 compositions according to the invention include: glycol ethers, such as, ethylene glycol dimethylether; propylene glycol dimethylether; glycol ether esters such as ethyl glycol acetate, butyl glycol acetate, 3-methoxy-n-butyl acetate, butyl diglycol acetate, methoxy propyl acetate, esters, such as, butyl acetate, isobutyl acetate, amyl acetate; ketones, such as, methyl ethyl ketone,
15 methyl isobutyl ketone; cyclohexanone, isophorone, aromatic hydrocarbons (e.g., with a boiling range from 136°C to 180°C) and aliphatic hydrocarbons. Chain transfer agents such as, e.g., mercaptans, thioglycolates, cumene or dimeric alpha methylstyrene may be used to control the molecular weight.

The hydroxyl groups of the hydroxy-functional (meth)acrylic copolymers
20 obtained in step A1) are modified at least partially with lactones (component d). This takes place by means of an esterification reaction, which proceeds with ring opening of the lactone. Again, hydroxyl groups are formed in the terminal position during the reaction.

The hydroxy-functional (meth)acrylic copolymers A) of the present
25 invention may be prepared by polymerizing the monomers a) to c) in step A1) in the presence of component d) or by polymerizing the monomers a) to c) in step A1) separately and then adding component d).

The two-component coating compositions of the present invention contain at least one polyisocyanate having free isocyanate groups as cross-
30 linking agents for the hydroxy-functional (meth)acrylic copolymers.

Examples of the polyisocyanates include any organic polyisocyanates having aliphatically, cycloaliphatically, araliphatically and/or aromatically

bound free isocyanate groups. The polyisocyanates are liquid at room temperature or liquefied by the addition of organic solvents. The polyisocyanates generally have a viscosity from 1 to 1 to 6,000 mPas at 23°C, preferably more than 5 and less than 3,000 mPas.

5 Polyisocyanates of this kind are known to the skilled person. The polyisocyanates are preferably polyisocyanates or polyisocyanate mixtures having exclusively aliphatically and/or cycloaliphatically bound isocyanate groups having an average NCO functionality from 1.5 to 5, preferably 2 to 4.

Particularly suitable examples are the so-called "coating
10 polyisocyanates" based on hexamethylene diisocyanate (HDI), 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexane (IPDI) and/or bis(isocyanatocyclohexyl)-methane and the inherently known derivatives of said diisocyanates having biuret, allophanate, urethane and/or isocyanurate groups from which, after their preparation, excess starting diisocyanate is
15 removed, preferably by distillation, to obtain a residual content of less than 0.5 wt-%. Triisocyanates such as nonane triisocyanate may also be used.

Sterically hindered polyisocyanates are also suitable. Examples thereof are 1,1,6,6-tetramethyl-hexamethylene diisocyanate, 1,5-dibutyl-penta-methyl diisocyanate, p- or m-tetramethylxylylene diisocyanate and the
20 corresponding hydrogenated homologues.

In principle, diisocyanates may be reacted in the usual way to higher functionality compounds, for example, by trimerization or by reaction with water or polyols, such as, e.g., trimethylolpropane or glycerin.

The polyisocyanate cross-linking agents may be used on their own or
25 in mixture. They are the conventional polyisocyanate cross-linking agents in the coating industry which are described comprehensively in the literature and are also available as commercial products.

The polyisocyanates may also be used in the form of isocyanate-modified resins.

30 The coating compositions of the present invention may contain additional hydroxy-functional binders apart from the hydroxy-functional (meth)acrylic copolymers A). For example, the additional hydroxy-functional

binders may be hydroxy-functional binders well known to the skilled person, of the kind used for the formulation of solvent-based coating compositions.

Examples of additional suitable hydroxy-functional binders include hydroxy-functional polyester, alkyd, polyurethane and/or poly(meth)acrylic resins which are different from the (meth)acrylic copolymers A). The additional hydroxy-functional binders may also be present in the modified form, e.g., in the form of (meth)acrylated polyesters or (meth)acrylated polyurethanes. They may be used on their own or in a mixture. The proportion of additional hydroxy-functional binders may be 0 to 50 wt-%, for example, based on the amount of hydroxy-functional (meth)acrylic copolymers A). The coating compositions may also contain low molecular weight reactive components, so-called reactive diluents that are capable of reacting with the cross-linking agent. Examples of these include hydroxy- or amino-functional reactive diluents.

The hydroxy-functional (meth)acrylic copolymers A) and the polyisocyanate cross-linking agents B) are used in each case in such quantity ratios that the equivalent ratio of hydroxyl groups of the (meth)acrylic copolymers A) to the isocyanate groups of the cross-linking agent is 5 : 1 to 1 : 5, for example, preferably, 3 : 1 to 1 : 3, particularly preferably, 1.5 : 1 to 1 : 1.5. If further hydroxy-functional binders and reactive thinners are used, their reactive functions should be taken into consideration when calculating the equivalent ratio.

The coating compositions according to the invention contain organic solvents. The solvents may originate from the preparation of the binders or they may be added separately. They are organic solvents typical of those used for coatings and well known to the skilled person, for example, those already mentioned above for the preparation of solution polymers.

The coating compositions according to the invention may contain pigments and/or fillers. Suitable pigments are all the conventional color-imparting and/or special effect-imparting coating pigments of an organic or inorganic nature.

The coating compositions may contain conventional coating additives. The additives are the conventional additives, which may be used, in the

coating sector. Examples of such additives include light protecting agents, e.g., based on benzotriazoles and HALS compounds (hindered amine light stabilizers), leveling agents based on (meth)acrylic homopolymers or silicone oils, rheology-influencing agents, such as, fine-particle silica or polymeric urea compounds, thickeners, such as, partially cross-linked polycarboxylic acid or polyurethanes, anti-foaming agents, wetting agents, curing catalysts for the cross-linking reaction, for example, organic metal salts, such as, dibutyltin dilaurate, zinc naphthenate and compounds containing tertiary amino groups such as triethylamine.

The hydroxyl group-containing binder component and the polyisocyanate component may be mixed together only shortly before application. In principle, the coating compositions may be adjusted with organic solvents to spray viscosity before application.

The coating compositions according to the invention may be applied by known methods, particularly by spraying. The coatings obtained may be cured at room temperature or by forced drying at higher temperatures, e.g., up to 80°C, preferably, at 20°C to 60°C. They may also, however, be cured at higher temperatures from, for example, 80°C to 160°C.

The coating compositions according to the invention are suitable for automotive and industrial coating. In the automotive coating sector, the coating agents may be used both for OEM (Original Equipment Manufacture) automotive coating and for automotive and automotive part refinishing. Stoving or baking temperatures from 80°C to 140°C, for example, preferably from 110°C to 130°C, are used for standard automotive coating. Curing temperatures from 20°C to 80°C, for example, particularly from 40°C to 60°C are used for automotive refinishing.

The coating compositions according to the invention may be formulated as pigmented top coats or as transparent clear coats and used for the preparation of the outer pigmented top coat layer of a multi-layer coating or for the preparation of the outer clear coat layer of a multi-layer coating. The present invention also relates, therefore, to the use of the coating compositions according to the invention as a top coat coating composition and

as a clear coat coating composition, and to a process for the preparation of multi-layer coatings, wherein, in particular, the pigmented top coat and transparent clear coat layers of multi-layer coatings are produced by means of the coating compositions according to the invention.

5 The coating compositions may be applied as a pigmented topcoat layer, for example, to conventional 1-component or 2-component primer surfacer layers. The coating compositions may be applied as transparent clear coat coating compositions, for example, by the wet-in wet method, to solvent-based or aqueous color- and/or special effect-imparting base coat
10 layers. In this case, the color- and/or special effect-imparting base coat layer is applied to an optionally pre-coated substrate, particularly pre-coated vehicle bodies or parts thereof, before the clear coat coating layer of the clear coat coating compositions according to the invention is applied. After an optional flash-off phase, both layers are then cured together. Within the context of
15 OEM automotive coating, flash-off may be carried out, for example, at 20°C to 80°C and within the context of refinishing over a period of 15 to 45 minutes at ambient temperature, depending on the relative humidity.

 The coating compositions of the present invention may be used as clear coat and topcoat coating compositions in automotive refinishing. Top
20 coat layers and clear coat layers with good scratch resistance and good hardness may be achieved in combination with an excellent physical drying performance.

 The invention will be explained in more detail on the basis of the examples below. All parts and percentages are on a weight basis unless
25 otherwise indicated.

Examples

Example 1

Preparation of a hydroxy-functional (meth)acrylic copolymer A1)

30 A four liter three-necked, glass flask equipped with an agitator, contact thermometer, dropping funnel and condensor was charged with 599.96 grams of Solvesso 100 (mixture of aromatic hydrocarbons, onset boiling point 164°C,

Exxon), 0.04 grams of dibutyltin dilaurate and 120 grams of butylacetate and heated to reflux at about 155°C. A monomer/initiator mixture consisting of 360 grams styrene, 360 grams isobornyl methacrylate, 1080 grams of hydroxypropyl methacrylate (mixture of isomers), 600 grams of epsilon caprolactone, 40 grams of di-tertiary-butylperoxide, 266.8 grams of Solvesso 100 and 53.2 grams of butylacetate were added continuously from the dropping funnel over 5 hours to the reactor contents. The dropping funnel was rinsed with 40 grams Solvesso 100 and the mixture refluxed till constant viscosity. The reactor contents were then diluted with 120 grams of Solvesso 100 and 360 grams of butylacetate.

The solids content were 59.9 % at a viscosity of I-1/4 Gardner-Holdt. The calculated hydroxyl value was 175 mg KOH/g, the acid value 4.2 mg KOH/g and the measured molecular weight (by Gel Permeation Chromatography using a polystyrene standard) was $M_n/M_w=1800/4700$. The caprolactone content was 25% on solids. The calculated hydroxyl value of the copolymer backbone was 233 mg KOH/g and the Tg of the copolymer backbone was 77°C, calculated according to the Flory-Fox equation (copolymer backbone = composition of copolymer without epsilon caprolactone).

Example 2

Preparation of a hydroxy-functional (meth)acrylic copolymer A2)

A four liter three-necked, glass flask equipped with an agitator, contact thermometer, dropping funnel and condensor was charged with 120 grams of n-butylacetate, 599.96 grams of Solvesso 100 (mixture of aromatic hydrocarbons, onset boiling point 164°C, Exxon) and 0.04 grams of dibutyltin dilaurate and heated to reflux at about 160°C. A monomer/initiator mixture consisting of 360 grams styrene, 432 grams isobornyl methacrylate, 360 grams of hydroxypropyl methacrylate (mixture isomers), 648 grams of 2-hydroxyethylmethacrylate, 600 grams of epsilon caprolactone, 53.2 grams of n butylacetate, 40 grams of di-tertiary-butylperoxide and 266.8 grams of Solvesso 100 were added continuously from the dropping funnel over 5 hours

to the reactor contents. The dropping funnel was rinsed with 40 grams Solvesso 100 and the mixture refluxed till constant viscosity. The reactor contents were then diluted with 480 grams of butylacetate.

The solids content were 59.5 % at a viscosity of M Gardner-Holdt. The
5 calculated hydroxyl value was 175 mg KOH/g, the acid value 3.4 mg KOH/g
and the measured molecular weight (by Gel Permeation Chromatography
using a polystyrene standard) was $M_n/M_w=1800/5400$. The caprolactone
content was 25% on solids. The calculated hydroxyl value of the copolymer
backbone was 233 mg KOH/g and the T_g of the copolymer backbone was
10 75°C, calculated according to the Flory-Fox equation (copolymer backbone =
composition of copolymer without epsilon caprolactone).

Example 3

Preparation of a hydroxy-functional (meth)acrylic copolymer A3)

15 A four liter three-necked, glass flask equipped with an agitator, contact
thermometer, dropping funnel and condensor was charged with 719.96 grams
of Solvesso 100 (mixture of aromatic hydrocarbons, onset boiling point 164°C,
Exxon) and 0.04 grams of dibutyltin dilaurate and heated to reflux at about
165°C. A monomer/initiator mixture consisting of 480 grams styrene, 552
20 grams isobornyl methacrylate, 360 grams of hydroxypropyl methacrylate
(mixture isomers), 648 grams of 2- hydroxyethylmethacrylate, 360 grams of
epsilon caprolactone, 80 grams of di-tertiary-butylperoxide and 266.8 grams
of Solvesso 100 were added continuously from the dropping funnel over 5
hours to the reactor contents. The dropping funnel was rinsed with 40 grams
25 Solvesso 100 and the mixture refluxed till constant viscosity. The reactor
contents were then diluted with 480 grams of butylacetate.

The solids content was 64.9 % at a viscosity of R+1/3 Gardner-Holdt.
The calculated hydroxyl value was 175 mg KOH/g, the acid value of 3.5 mg
KOH/g and the measured molecular weight (by Gel Permeation
30 Chromatography using a polystyrene standard) was $M_n/M_w=1300/3000$. The
caprolactone content on binder solids was 15%. The calculated hydroxyl
value of the copolymer backbone was 205 mg KOH/g and the T_g of the

copolymer backbone was 80°C, calculated according to the Flory-Fox equation (copolymer backbone = composition of copolymer without epsilon caprolactone).

Example 4 (Comparative example)

5 Preparation of a hydroxy-functional (meth)acrylic copolymer A4)

A four liter three-necked, glass flask equipped with an agitator, contact thermometer, dropping funnel and condensor was charged with 719.96 grams of Solvesso 100 (mixture of aromatic hydrocarbons, onset boiling point 164°C, Exxon) and 0.04 grams of dibutyltin dilaurate and heated to reflux at about
10 165°C. A monomer/initiator mixture consisting of 360 grams styrene, 552 grams isobornyl methacrylate, 360 grams of hydroxypropyl methacrylate (mixture of isomers), 576 grams of 2- hydroxyethylmethacrylate, 360 grams of epsilon caprolactone, 80 grams of di-tertiary-butylperoxide and 266.8 grams of Solvesso 100 were added continuously from the dropping funnel over 5
15 hours to the reactor contents. The dropping funnel was rinsed with 40 grams Solvesso 100 and the mixture refluxed till constant viscosity. The reactor contents were then diluted with 480 grams of butylacetate.

The solids content was 61% at a viscosity of E+1/2 Gardner-Holdt. The calculated hydroxyl value was 155 mg KOH/g, the acid value 3.6 mg KOH/g
20 and the measured molecular weight (by Gel Permeation Chromatography using a polystyrene standard) was $M_n/M_w=1400/3400$. The caprolactone content on binder solids was 25%.

The calculated hydroxyl value of the copolymer backbone was 205 mg KOH/g and the T_g was 80°C, calculated according to the Flory-Fox equation
25 (copolymer backbone = composition of copolymer without epsilon caprolactone).

Example 5 (Comparative Example)

30 Preparation of a hydroxy-functional (meth)acrylic copolymer A5) according to EP 1201690

A 4 liter three-necked, ground glass flask fitted with an agitator, contact thermometer, dropping funnel and spherical condenser was charged with 720

grams of Solvesso 100 (mixture of aromatic hydrocarbons, onset boiling point 164°C, Exxon) and heated to 164°C with stirring and reflux cooling. A monomer/initiator mixture of 480 grams of styrene, 3960 grams of hydroxypropyl methacrylate, 600 grams of isobornylmethacrylate, 360 grams of glycidyl methacrylate, 80 grams of di- tertiary butylperoxide and 280 grams of Solvesso 100 were added continuously from the dropping funnel over a period of 5 hours. After the addition, the monomer-mixing vessel and the dropping funnel were rinsed with 40 grams of Solvesso 100 and the contents added to the reaction mixture. The reaction mixture was held at reflux for one more hour before cooling with 480 grams Solvesso 100. The resulting polymer solution had a solids content of 60.2% at a Gardner-Holdt viscosity of T+1/2 and a molecular weight distribution of Mn/Mw = 1250/3000.

In another reactor setup as described above, 8.5 parts of dimethylolpropionic acid were refluxed in 6.1984 parts of n-butylacetate, 0.0016 parts dibutyltin dilaurate and 22.8 parts of epsilon caprolactone for 6 hours. Next, 100 parts of the above polymer solution were added, followed by the addition of 0.014 parts tetraethylammoniumbromide and 0.986 parts n-butylacetate. This mixture was refluxed till the acid value remained constant before diluting with 2 parts of n-butylacetate.

The final solids content of the graft copolymer was 69% with a viscosity of W+1/4 at an acid value of 6.7 mg KOH/g, a calculated hydroxyl value of 175 mg KOH/g and molecular weight distribution of Mn/Mw = 1400/3900. The caprolactone content on binder solids was 25%.

Example 6 (Comparative Example)

Preparation of a hydroxy-functional (meth)acrylic copolymer A6), prepared according to the method described in EP1227113

A reaction product of 26.8 parts hydroxypropyl methacrylate and 15 parts of epsilon caprolactone was prepared by heating above mixture in 6 parts Solvesso 100 with 0.02 parts di-tertiary butyl hydroxy toluene (BHT) and 0.001 parts of dibutyltin dilaurate at 110-120°C for 8 hours while air is purged in the reaction mass. In a next step, a copolymer was prepared as in

Example 1 in a reactor setup as described above by adding over a 5 hour period a mixture of 360 grams styrene, 360 grams isobornyl methacrylate, 1920.84 grams of the hydroxypropyl methacrylate-epsilon caprolactone reaction product solution above, 40 grams of di-tertiary butylperoxide, 25.2 grams of Solvesso 100, 53.2 grams of n-butylacetate to a reactor with a blend of 600 grams Solvesso 100 and 120 grams of n-butylacetate at 155°C reflux temperature. The addition funnel was rinsed with 40 grams of Solvesso 100 and the reactor contents held for 1 hour at reflux temperature before thinning down with a blend of 120 grams of n-butylacetate and 360 grams of Solvesso 100.

The solids content was 54.1 % at a viscosity of F-1/4 Gardner-Holdt. The calculated hydroxyl value was 175 mg KOH/g, the acid value was 3.8 mg KOH/g and the measured molecular weight (by Gel Permeation Chromatography using a polystyrene standard) was $M_n/M_w = 1700/4500$. The caprolactone content was 25% on solids. The calculated hydroxyl value of the copolymer backbone was 233 mg KOH/g and the Tg of the copolymer backbone was 77°C, calculated according to the Flory-Fox equation (copolymer backbone = composition of copolymer without epsilon caprolactone).

Example 7

Preparation of coating compositions

Two-component clear coats were prepared based on the hydroxy-functional (meth)acrylic copolymers A1) to A6) according to Examples 1-6 (component I) and based on a polyisocyanate cross-linking agent (component II). The components I and II were prepared as follows:

CC = clear coat

Comp. CC = comparative clear coat

<u>Components I</u>	Standard CC	CC1 / Example 1	Comp. CC 6 / Example 6
Methyl isobutyl ketone	4.47	5.56	
Amyl acetate	2.36	3.25	0.98
Ethyl 3-ethoxypropionate	3.43	4.72	4.21
Alkylene glycol alkylether acetate	2.41	3.32	2.38
Levelling agent (polyether modified polysiloxane)	0.10		
Levelling agent (polyester modified polysiloxane)		0.05	0.05
Levelling agent (polyacrylate)	0.2	0.33	0.33
Dibutyl tin dilaurate (1% solution)	1.49	0.87	0.87
Light stabilizer (HALS)	0.3	0.76	0.76
UV absorber	0.6	1.52	1.52
Diethyl ethanol amine	0.25	0.29	0.29
Acrylic copolymer standard (1)	83.29		
Acrylic copolymer Example 1 (59.9%)		78.13	
Acrylic copolymer Example 6 (54.1%)			88.26
Acetic acid	0.3	0.35	0.35
Butylacetate	0.8	0.85	
Total	100	100	100

- (1) Acrylic Copolymer standard – 47.7% solids of an acrylic polymer of styrene/methylmethacrylate/hydroxy ethylmethacrylate/acrylic acid – Cardura® E IO (glycidyl ester of a versatic acid having 10 carbon atoms in the acid molecule), having a weight average molecular weight Mw of 6,000 and OH value of 1444 mg KOH/g.

<u>Compon nts I</u>	CC2 / Example 2	CC3 / Example 3	Comp. CC4 / Example 4	Comp. CC5 / Example 5
Methyl isobutyl ketone	7.74	7.74	7.74	7.74
Amyl acetate	4.52	4.52	4.52	4.52
Ethyl 3-ethoxypropionate	6.57	6.57	6.57	6.57
Alkylene glycol alkylether acetate	4.61	4.61	4.61	4.61
Levelling agent (polyester modified polysiloxan)	0.05	0.05	0.05	0.05
Levelling agent	0.3	0.3	0.3	0.3
(poylacrylate)	0.8	0.8	0.8	0.8
Dibutyl tin dilaurate (1% solution)	0.7	0.7	0.7	0.7
Light stabilizer (HALS)	1.4	1.4	1.4	1.4
UV absorber	0.27	0.27	0.27	0.27
Diethyl ethanol amine				
Acrylic copolymer Example 1 (59,9%)	71.92			
Acrylic copolymer Example 3 (60% in butylacetate)		71.92		
Acrylic copolymer Example 4 (60% in butylacetate)			71.92	
Acrylic copolymer Example 5 (60% in butylacetate %)				71.92
Acetic acid	0.32	0.32	0.32	0.32
Butylacetate	0.8	0.8	0.8	0.8
Total	100	100	100	100

All figures in the tables above are weight-%. In addition, for comparison purposes a standard clear coat based on the acrylic copolymer standard (1) has been applied.

5 **Component II**

14.8 parts by weight of xylene, 18.5 parts by weight of butyl acetate, 1.4 parts by weight of ethylacetate, 65.3 parts by weight of a commercially available polyisocyanate (Desmodur® 3390/Bayer) were mixed homogeneously to obtain the solution of curing agent.

10 Component I and component II were mixed in each case homogeneously in amounts to achieve a OH/NCO ratio of 1.05 in the coating composition.

Application of the clear coat compositions

15 Standard metal panels, on which a commercial primer and a commercial solvent borne basecoat has been applied, were coated with the clear coats from Examples 1-6. The clear coats were applied in a dry film thickness of 50 µm and hardened for 30 minutes at 60°C (horizontally) after 10 minutes flash-off at room temperature.

20 The coating results are shown in the following tables:

	Standard CC	CC1 / Example 1	Comp. CC6 / Example 6
<u>Appearance</u>	Clear	Clear	Clear
<u>Drying time</u> : tape free initial /recovered	VVP / F	F / Ex	P-F/Ex
<u>Fischer hardness</u> (initial / after 1 week)	0.2 / 13.8	0.1 / 12.0	0.16/11.4
<u>Perzos hardness</u> (initial / after 1 week)	58 / 300	35 / 280	41/270
<u>Scratch</u> (gloss before / after scratching)	91.1 / 42.6	85.5 / 73.1	86 / 61.8

	CC2/ Example 2	CC3 / Example 3	Comp. CC4 / Example 4	Comp. CC5 / Example 5
<u>Appearance</u>	Clear	Clear	Clear	Clear
<u>Drying time</u> : tape free init./recov.	VP / VG 0.14 / 7.2	VVP/P 0.18/8.8	VP/G 0.1/3.1	VVP/P NM/5.4
<u>Fischer hardness</u> (initial / 1 week)	33 / 204 88 / 67	34/209 86/33.7	26/136 86/33.7	NM 87/69
<u>Perzos hardness</u> (initial / 1 week)				
<u>Scratch</u> (gloss before / after scratching)				

NM – not measurable

Test methods used:

5 Drying / tape free initial:

After a 10 minute cool-down period after baking, a strip of masking tape was applied across the panel, smoothing it out manually using moderate firm pressure to insure uniform contact. A 2 kg weight was rolled over the tape to and from. After 10 minutes, the tape was removed and the degree of marking was observed. After 30 minutes recovery, the tape imprint was evaluated again.

Ratings: VVP - very very poor, VP - very poor, P - poor, F - fair, G - good, VG - very good, Ex - excellent

15 Scratch Resistance:

The clear coated panels were scratched after 7 days aging using the linear Gardner brush test (nylon brush) (according to ASTM D2486-89) through using an abrasive medium based on calcium carbonate. Each panel undergoes 30 brush cycles. The gloss before and after scratching was measured.

The clear coats according to the invention show better overall results in comparison to the comparative clear coats. Scratch resistance has been increased remarkably compared with the standard clear coat, while maintaining a very good hardness. Compared with comparative clear coat 6,
5 a better drying performance (tape free initial) and improved scratch resistance have been achieved.

Compared with comparative clear coat 4, hardness and scratch resistance have been improved remarkably. Comparative clear coat 5 shows good scratch resistance but very poor drying performance and unacceptable
10 hardness.